CHROMATE FILM USED FOR CHEMICAL CORROSION CONTROL ON GOLD-PLATED PCB CONNECTORS

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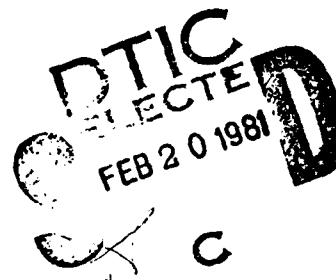
Electrical intermittencies in nuclear submarine navigational computers can result from degra-
dation of gold-coated contacts by insulating films, the latter identified as principally composed
of organics and silver sulfide. The films can be removed, but without appropriate measures, they
recur. To retard insulating film build-up, a protective, noninsulating chromate surface treatment
was developed; it has proven effective in extending service life. Because protection arises from a
surface modification, investigation of the chromating process requires the use of surface-sensi-
tive techniques. Analysis by AES, SAM, XPS, EMA and RBS reveals the presence of a thin
(< 30 Å) layer, rich in Cr^{3+} on top of the gold. This contrasts with much thicker films incorpo-
rating Cr^{6+} species found in chromate films grown for the protection of Zn, Cd and Al. The ab-
sence of Cr^{6+} species suggests the chromate film on gold protects via a physical rather than elec-
trochemical mechanism. The chromate film continuity and composition can be adversely affect-
ed by mechanical contact, tarnish growth, and substrate microheterogeneity. Copper compounds
are implicated in the occasional development of insulating films during field application of the
chromate treatment.

1. Introduction

A major source of unreliability in navigational computers on nuclear submarines
is the electrical intermittents associated with poor contacts of the printed circuit
boards (PCB's) in the wire harnesses and within the computer itself [1,2]. During
periods of prolonged submergence, the submarine must rely on navigational equip-
ment which functions with no active input from terrestrial sources. Its guidance
system includes gyros and accelerometers which provide data to an on-board Marine
Digital Analyzer (MARDAN) computer. Intermittencies, taking the early form of
electrical noise in the data linkages, have been traced to the presence of dirt, tarnish,

corrosion products and organic contaminants accumulating at the male (PCB)/female connector pin junction.

Initial examination of the deleterious contaminant film by electron microprobe and infrared spectroscopy showed the presence of Ag, S and organic material. The latter was identified as trigylcerides and probably originates from galley greases. Subsequent examination by Auger spectroscopy revealed that films which show up as black deposits are predominantly carbonaceous in character and have increasing amounts of Ag and S as the deposit is etched away. The lineshape of the sulfur is consistent with sulfide [3]. There are other films which show a silvery appearance; AES examination shows these to differ from the black deposits principally through smaller amounts of carbonaceous material.

The bellow-form spring female pins (fig. 1) in the electrical connectors are fabricated principally from a resilient beryllium—copper alloy, but rely for their corrosion protection on the thin surface coatings shown in the cross-section. The purpose of the gold plate is to prevent tarnish formation by the silver and thereby maintain a contact surface of low resistance. However, it is well known that defects in the Au film can lead to formation of silver sulfide with subsequent rapid migration across the gold surface [4,5,6]. This tarnish is forming on the MARDAN contacts and its deleterious effect is augmented by the presence of accumulated organic material.

The most obvious solution for reducing the tarnish is to replace the connector pins with new ones which have no silver between the copper and its gold coating. In fact, new female connectors for use in the MARDAN unit do not contain the silver layer. However, the cost of a retrofit is prohibitively expensive. Rather, some preventative measure amenable to application to the in-place connectors had to be developed. One such measure, based on chromate conversion technology, has been developed and proven effective in extending useful service life [1]. The present work examines some of the phenomena associated with this treatment.

Chromate conversion coatings are utilized for corrosion prevention by the metal finishing industry [7]. The chromate conversion process consists of briefly immers-

CONNECTOR PINS

Au (< 0.8 μm)

Ag (15 μm)

STRIKE (0.8 μm) (optional)

Be–Cu SUBSTRATE

CROSS-SECTION

SINGLE PIN

MOLDED PAIR
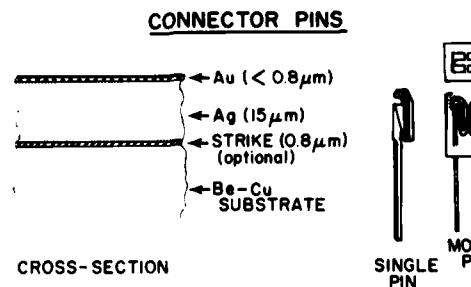
Fig. 1. Composition (in cross-section) and configuration of female connector pins.
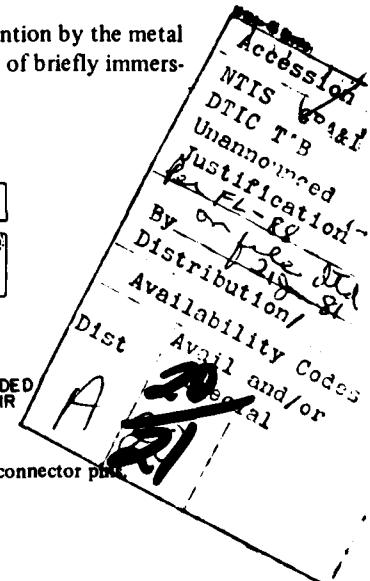
ing the reactive metal needing protection with an acidic solution of a chromate compound. Some metal dissolves into the etchant, forming positive metal ions and releasing electrons. The electrons serve to reduce the Cr^{6+} to Cr^{3+} and also to increase the local pH (i.e., the solution immediately adjacent to the metal surface becomes less acidic). As the pH increases, a gel precipitates on the surface. This so-called "chromic chromate" [7] appears to be a mix of chrome oxide, Cr_2O_3, chrome hydroxide, $Cr(OH)_3$, some Cr^{6+} species, water and possibly other ions. The film composition has been studied on Al with AES, XPS, and IMMA for several chromate coating solutions by Katzman et al. [8]. They find film thicknesses on the order of a thousand Ångströms, a trivalent to hexavalent chromium ratio of about 2:1 and some Al incorporated into the film.

A metal surface, having been "converted" from reactive metal to protective film, derives its protection via two mechanisms [7,9]: (i) the chrome oxide and hydroxide constituents, which make up most of the film, form a physical barrier to corrosive attack of the metal substrate; and (ii) the Cr^{6+} precipitated in the gel can, providing the film remains sufficiently hydrous, migrate to any flawed area and there produce a passive layer. The films are thus potentially self-healing.

There are two issues associated with the use of a chromate conversion coating for the protection of MARDAN connector pins for which surface analysis has proven useful. First, the protective film needs to be examined to identify the nature of the passivation — i.e., physical and/or chemical. Second, the surface composition factors influencing film growth must be identified so that they may be better controlled. The chromating process does not form a deposit on Au by itself. It has been used for protection of Ag and Cu [10,11] and can provide protection against corrosion of gold-plated Ag and Cu [1,6,12,13]. Chromate film growth depends on a set of complex electrochemical reactions. The potentials which control these reactions are sensitive to the bi-(Ag/Au) or tri-(Cu/Ag/Au) metallic couples and to contamination. Since the contacts must retain low contact impedance as well as corrosion resistance, control of the factors affecting film growth is important. This point will be illustrated by two examples.

2. Experimental procedure

The XPS and most of the AES work cited here were performed on pure Au or Ag coupons or on rectangular coupons of BeCu alloy which had been electroplated with Ag or Au. For the bimetallic couple, one half of a silver-plated coupon was overplated with gold. The Ag plate thickness of 25 μ was deposited from a high-speed, bright silver bath, "Techni-Silver E" (Technic, Inc.), after a deposition of potassium cyanide silver strike. Those samples which were to be overplated with gold were then buffed. The gold bath used was a commercially prepared (KCN Type) 24 KT known for producing plate of high ductility and tight grain structure; the current density and plating time were adjusted to deposit 0.6 μ of gold. These thick-

nesses correspond to those found on the MARDAN female connector pins.

The coupons were cleaned by successive ultrasonic exposure to toluene, Freon and methanol. The chromate films were grown by submersion of the cleaned metal surfaces in a 2% solution of "Kenvert 31" (Conversion Chemical Corporation), modified as indicated in ref. [1] and adjusted to pH 1.8 ± 0.2 with NaOH. Standard immersion periods of 3 min were used in this study, consistent with the 2–5 min treatment time specified for refurbishing of MARDAN assemblies.

Most Auger spectra were acquired from a Physical Electronics Industries Model 545 Scanning Auger Microprobe using a 5 μm diameter beam; however, the set of elemental maps shown in fig. 4 was acquired on the Model 590 with the increased spatial resolution afforded by a 0.7 μm diameter beam. A 2 keV Ar ion gun was used to obtain depth profile information; the ion current density was measured to be 18 μA/cm^2. The XPS data were acquired with a Physical Electronics Industries double-pass CMA operating in the retard mode with pass energy of 50 eV. An Al anode X-ray source was used. The binding energies were referenced to an Au $4f_{5/2}$ binding energy of 83.8 eV.

3. Results and discussion

3.1. Studies of chromate films on reference samples and connectors

In order to be effective in retaining low contact impedance while preventing Ag tarnish on the electrical connectors, the chromate film growth must not result in a thick film on top of the Au plate, but at the same time must somehow protect any defect in the Au which exposes Ag. Pure Au alone is not expected to show any film formation via the chromating process. Tests on bulk Au showed that some chromate film did deposit. The small amount, estimated to be less than a monolayer (see fig. 2), may have been caused by Ag known to be present as a contaminant in the Au sample. A pure silver sample, on the other hand, showed considerable film growth as shown by its depth profile in fig. 2. The sputter rate of the chromate-induced film is not known, but a sputter rate of 7 Å per μA·min/cm^2 has been reported for Cr$_2$O$_3$ grown by air exposure of clean chromium metal surfaces and bombarded with 3.0 keV argon ions [14]. An Ag AES signal intensity was detected throughout the depth profile and grew stronger as the film etched away. While this could be interpreted as increasing exposure of thinly covered Ag islands, it is more likely that Ag is incorporated into the film; Katzman et al. [8] observed similar incorporation of Al in chromate films grown on that metal.

The chromate films formed by the exposure of a pure metal are not necessarily equivalent to the films formed when a bi- or tri-metallic couple is present. The different electrochemical potentials of the Au and Ag will cause the Au to become cathodic and one might expect increased film growth on top of the Au, the thickness depending on the relative areas of Au to Ag and the growth time. This pheno-
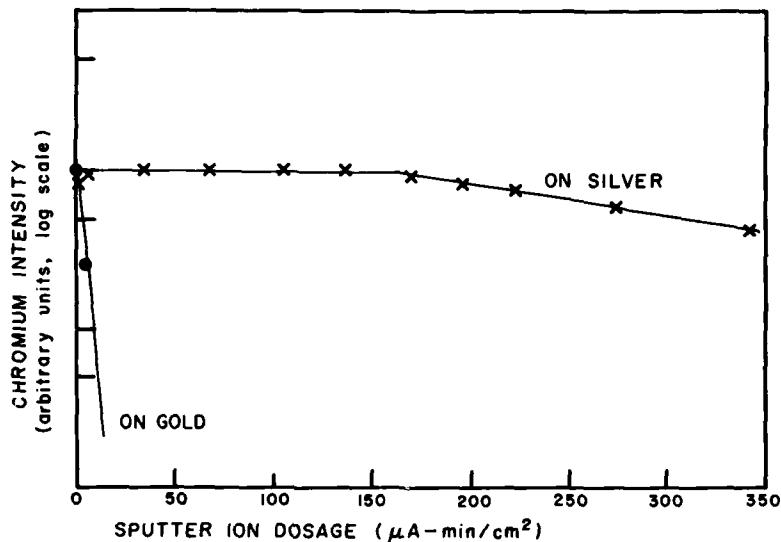
Fig. 2. Auger sputter profile of chromate films on pure metals.

menon has been confirmed by Auger examination of the chromate film formed on the coupons with the bimetallic Au/Ag couple. The film thickness on the Au increased compared to pure Au, while that on the Ag decreased compared to pure Ag. Measurements of chromate films grown on actual connector pins where Ag is exposed only through flaws in the Au plate show film thickness on the Au on the order of 20 Å.

The AES data on the chromate films show that the chromating process can mask exposed Ag without growing undue film thicknesses on the Au. Tests of chromated coupons and actual connector pins confirm that the chromated samples are less susceptible to tarnish formation in a humid, sulfide environment [1,12].

The chromate conversion coatings on Al were shown by XPS to contain large amounts of Cr^{6+} [8]. This species is believed to be essential for the coatings to heal any rupture. The chromate films grown as part of this study were also examined by XPS. The literature on chromium oxides binding energies shows binding energies of 579.3 for Cr^{6+}, 576.6 for Cr^{3+} in Cr_2O_3, and 577.0 eV for Cr^{3+} in $Cr(OH)_3$ [15,16]. There was no evidence of Cr^{6+} species in any of the films grown on the pure metal or bimetallic coupons. (See fig. 3 for representative spectra.)

The absence of Cr^{6+} in the chromate film formed on the model Au/Ag samples suggests that flaws in the chromate film would not be able to heal and therefore would be susceptible to corrosive attack. A major factor is the mechanical abrasion suffered by the contacts during use. Deep, linear gouges are visible on the contact
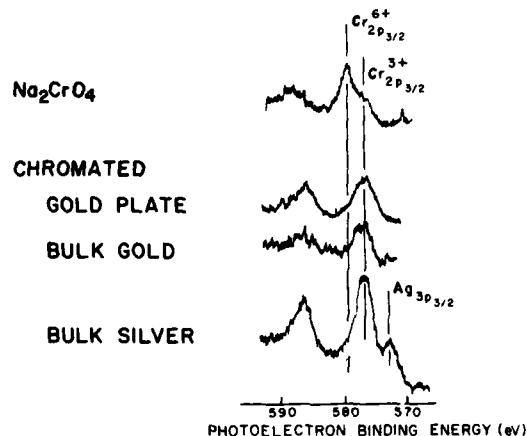
Fig. 3. Chromium $2p_{3/2}$ and $2p_{1/2}$ X-ray photoelectron binding energies from sodium dichromate solution evaporated on gold and from chromate films formed on indicated substrates by exposure to the chromating procedure.

areas of disassembled MARDAN female connectors. SAM examination of these scratches shows that not only can the Au plate be penetrated, but even the much thicker Ag layer. By introducing additional micro-sites with potential for electrochemical reactions at the exposed bi-metallic couples, such penetration increases the vulnerability of the scratch to corrosive attack. As expected for such deep gouges, the chromate-grown overlayer has been removed and has not regrown, despite the SAM evidence of a strong Cr presence external to the scratch.

3.2. Factors influencing chromate film growth

The chromate film growth depends on the local electrochemical potentials. When extraneous sources of potential are present, such as metallic contaminants, the film may not form a protective barrier. This is exemplified in the micrographs of fig. 4, taken from a visibly discolored area ($\approx 0.08 \times 0.2$ mm) on a chromated Au over Ag over Cu strike on a Be—Cu substrate reference specimen which had been exposed to an accelerated sulfide corrosion test. Despite the chromating, small areas of tarnish had developed within 2 h exposure to 0.5 ppm ammonium sulfide vapor. Fig. 4 is a composite of two types of SEM images plus a set of elemental maps all obtained at the same magnification using a fine beam (diameter $\approx 0.7\ \mu$). The central feature is a hairline crack only about 10 μ long.

There is a strong correspondence between the SEM details and the SAM maps showing elemental distribution. Thus, the featureless area (bright gold to the eye) consists of a relatively homogeneous distribution of such expected elements as gold

(a) SECONDARY ELECTRON DISPLAY   (b) ABSORBED CURRENT IMAGE

(c) ELEMENTAL DISTRIBUTION (SCANNING AUGER IMAGE)
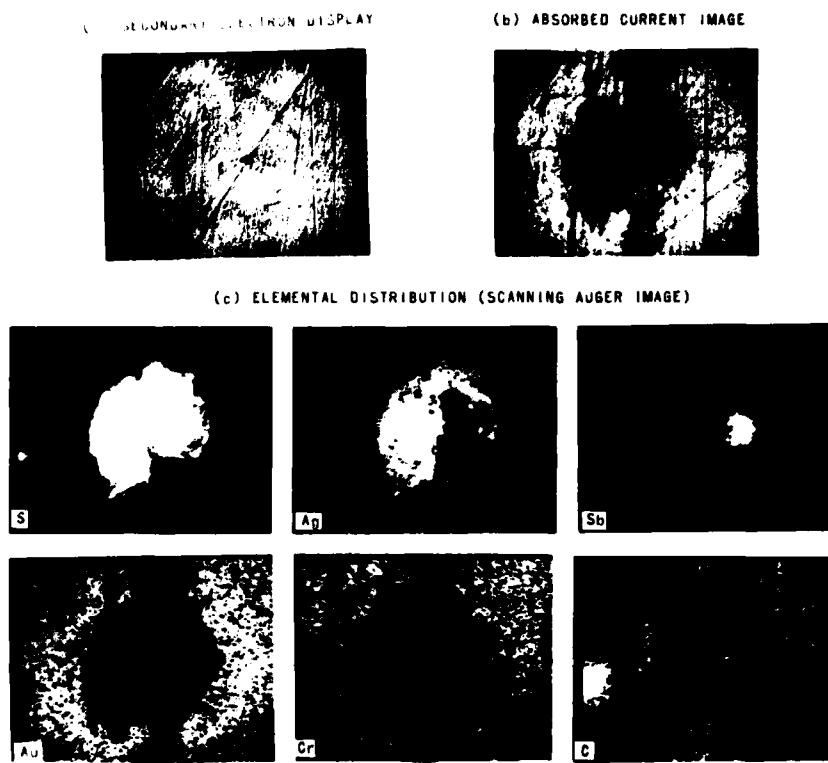
Fig. 4. Scanning electron micrographs and scanning Auger electron images of a discolored area on a chromated, gold-over-silver plated specimen, which had been stored for three months after limited exposure to a sulfide atmosphere. (Marker indicates 20 μm.)

and chromium, together with a carbonaceous overlayer. The mottled area in the SEM shows a one-to-one correspondence with the sulfur distribution, this concentration being greatest at and immediately adjacent to the hairline crack. This is also the region of highest concentration of silver, suggesting that the silver had erupted at the crack and had spread from there, reacting with sulfur from the atmosphere and forming the discoloring tarnish.

Although the strongest sulfur signals correlated with the area containing surface-exposed silver, the correspondence was not complete. A semi-circular area (about in its largest dimension) existed for which there was no corresponding concentration of any of the elements expected from either the electroplating or chromating processes. A static multi-element AES trace indicated the unexpected constituent as antimony. SAM mapping for this element (Sb in fig. 4) showed it to be local-

ized precisely to the semi-circular area. The proximity to the hairline crack suggests an origin within the undercoating rather than the gold-plated outer surface. The evidence suggests that the presence of the antimony prevented the chromate film from sealing of this pore to silver sulfide migration.

In contrast to the above example of incomplete film formation, the growth of chromate films in field applications is occasionally marred by the deposition of thick, insulating films. These occur as discolored layers visible as soon as the connectors are rinsed free of the chromating solution. They can be removed by repeating the cleaning and detarnishing steps and usually do not recur on rechromating, but this slows the refurbishing process. Field-generated insulating films have therefore been studied to identify and eliminate their cause.

The insulating films are sufficiently thick to be visible; therefore it is not surprising that no Auger signal can be detected from the subjacent gold coating. As shown in the Auger depth profile of fig. 5, the chrome content is low prior to inert-ion sputtering; also present, and in an initial concentration greater than that of chrome, is copper. When sputtering is initiated, the carbon content reduces and the copper content rises sharply; the effect of sputtering on the Cr and O content, however, is a much more gradual increase. As shown by the depth profile, the copper tends to be localized toward the outermost surface, with continued sputter-etching reducing the Cu to a low level.

It thus appears that the copper is directly related to gross film formation, not as an integral constituent of the chromate film but rather as a promoter of the film formation. Empirical studies have shown that the presence of Cu salts, $CuCl_2$ in particular, at the contacts during the chromating process do in fact stimulate excess film growth. Given the built-in source of copper (e.g., the substrate material for both male and female contacts) and the active nature of the submarine atmosphere,
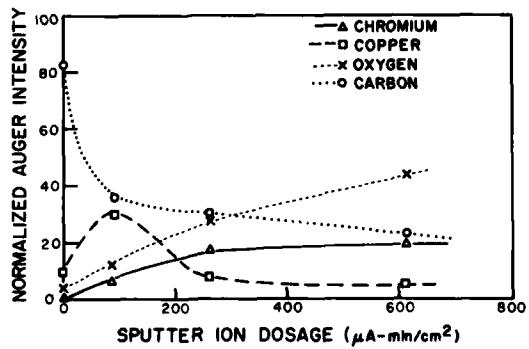

Fig. 5. Auger sputter profile of the insulating film which developed during field application of the chromating process to used, male PCB connectors.

the formation of such potentially deleterious species is obviously favored by conditions in the MARDAN/submarine system. For example, male PCB contacts are fabricated by pattern-plating gold onto copper-clad epoxy/glass laminates and then etching away the unwanted metal. Copper is thus exposed along the edges of all contact fingers and may also be made available at flaws in the gold and by migration through the gold. Corrosion of the exposed copper is then promoted by the presence of high humidity, periodic condensed moisture, and the presence of sodium chloride (residues from the salt mist introduced by the main ship's fans into the air-conditioning intake to the electric console) [2].

In view of the evidence implicating copper compounds in insulating-film formation, questions arise as to whether the copper is a surface constituent because the gold plating has been eroded by usage. RBS experiments were performed using both 2.0 and 3.0 MeV He^4 and 3.0 MeV H^+ beams on both normal, transparent, non-insulating chromate films and on thick, brown films found on adjacent male fingers on a single PCB. The higher energy alpha particles sample the surface to a much greater depth (40 μ). Both techniques indicated gold thicknesses of 1.3 μ, with less than a 2% discrepancy between the transparently coated gold connector and the seriously discolored contact, thus indicating that the gold had not been eroded in the latter case. The 3.0 MeV He^4 beam did show a small peak in the position associated with a surface layer of Cu on the discolored finger.

The electron microprobe (EMA) was then employed to analyze the thick film deposits because (i) it provides the lateral resolution unobtainable by RBS, and (ii) its response is limited to the outermost one micron of the surface. Thus, any copper detected by EMA must have its origin within or on top of the gold coating. On both the bright gold and brown-film coated fingers there was found a uniform coverage of copper. Despite the use of magnifications of 20000X, there was no evidence either of pores in the gold coating or of copper migrating along localized channels in the gold. Comparison of the clear with the discolored areas indicated that the copper concentration was lower and both the Cr and Au concentrations were higher on the gold-colored area than on the discolored areas, in agreement with the AES data.

Thus, all of these techniques indicate that higher copper concentrations are found in the discolored areas. There is no evidence linking the presence of copper to migration through pores or imperfections in the front surface of the gold coating in a manner analogous to the Ag migration on the female connector pins.

4. Summary

Studies on plated metal reference systems and on commercially available gold-plated PCB connectors, both male and female, show that non-insulating, protective films can be formed by modified chromate treatment. Analysis of such films by AES, SAM, XPS, EMA and RBS reveals the presence of a thin (< 30 Å) layer, rich in Cr^{3+}, on top of the gold. This contrasts with much thicker films incorporating Cr^{6+} species found in chromate films grown for the protection of Zn, Cd and Al.

The absence of Cr^{6+} species suggests the chromate film on gold protects via a physical rather than electrochemical mechanism.

The chromate film continuity and composition can be adversely affected by mechanical contact, tarnish growth, and substrate microheterogeneity. Copper salts are implicated in the occasional development of insulating films during field application of the chromate treatment to used, male PCB connectors. Inasmuch as no evidence was obtained for migration of copper through the gold coating, the most likely source of the interfering copper compounds is from submarine-atmospheric attack on copper exposed at the edges of the contacts.

Acknowledgement

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